



Direct Analysis of Milk Powder by Axially-Viewed Simultaneous ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Authors

Andrew Tame
Dennis Hoobin

Introduction

The elemental analysis of milk is important both as an indicator of environmental contamination and because milk is a significant pathway for toxic metal intake and a source of essential nutrients [1] for humans.

The accepted methods for elemental analysis of milk have traditionally included either wet digestion or dry ashing [3–6]. These are time consuming and involve procedures using potentially hazardous chemicals. A direct method of analysis by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES) would obviously be preferable, but this relies upon the instrument tolerating high levels of dissolved solids while providing sufficient sensitivity to measure toxic trace elements and the dynamic range to measure nutritional major elements.

The use of a sequential ICP-OES for direct analysis of milk has been previously described by Ryan [2]. This work describes the direct analysis of milk powder using standard quantitative calibration with aqueous standards using a simultaneous ICP-OES system. Viscosity effects of the milk powder solutions are corrected using scandium (361.383 nm—ionic line) as an internal standard. Major, minor and trace elements were determined in a single analysis. Less sensitive lines are used for the determination of major elements allowing both major and minor elements to be determined from a single solution.

Many of the major constituents in milk powder such as Na, K and Ca are Easily Ionized Elements (EIE) which can cause ionization interferences. Previous work [2] has shown that the addition of caesium as an ionization suppressant and internal standard to the standards and samples was beneficial. The ionization suppressant and internal standards are conveniently introduced into the plasma on-line, via the third channel of the peristaltic pump. The accuracy and validity of the method was assessed by the use of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 8435 Whole Milk Powder.



Agilent Technologies

Experimental

Instrumental

The Vista simultaneous ICP-OES axially viewed plasma was used for the analysis. The Vista features a free running, air cooled, 40 MHz RF generator and cooled cone interface. The Vista's optical system is based on an echelle polychromator with Charged Coupled Device (CCD) detector. The polychromator is thermostatted to 35 °C for stability, and the unique CCD detector features 70,000 pixels (detectors) arranged to exactly match the 2 dimensional echellogram. Sophisticated design of the detector has resulted in a rapid readout with excellent detection limits [4]. The instrument was controlled by an IBM computer with an Intel Pentium processor and Agilent's Vista worksheet software running under Microsoft's Windows NT operating system.

In this work a Vista with manual gas pressure regulator was used. Mass flow control of the nebulizer flow, which allows the nebulizer gas flow to be automatically adjusted, is available as an option. This work took advantage of the third channel pump to add internal standard and ionization suppressant on line. The Vista instrument is available with either the two or three channel pump option.

Table 1. Instrument Operating Conditions

| | |
|-----------------------|----------------------------------------------|
| Power | 1.35 kW |
| Plasma gas flow | 15.0 L/min |
| Auxiliary gas flow | 1.5 L/min |
| Spray chamber type | Sturman-Masters |
| Torch | Standard axial torch with 2.3 mm id injector |
| Nebulizer | V-groove |
| Nebulizer pressure | 240 kPa |
| Pump tube Inlet | PVC black-black |
| Outlet | PVC, blue-blue, 1.65 mm id |
| Polychromator purge | Boost (3.7 L/min) |
| Pump speed | 15 rpm |
| Sample uptake rate | 0.6 mL/min |
| Integration time | 3 seconds |
| No. of replicates | 3 |
| Sample delay time | 20 seconds |
| Fast pump | On |
| Stabilization time | 20 seconds |
| Background correction | Fitted, 2 points/peak |

To make sure that the milk powder sample was evenly mixed and in suspension while being aspirated, the solution was continuously stirred with a magnetic stirrer. Sodium and

potassium were internally standardized with the caesium 372.328 nm line, using added caesium as both the ionization suppressant and internal standard. Scandium was used as an internal standard for all other lines.

Standard Preparation

Aqueous standards were prepared from 1000 mg/L single element standards (Spectrosol, BDH Chemicals). The standards were made up in 18 M Ω Milli-Q water with 0.5% v/v HNO₃ and 0.002% v/v Triton X100 prepared from a 1% w/v Triton X100 solution.

Table 2. Calibration Standards Prepared

| Standard | Elements and concentration (mg/L) |
|-------------|--------------------------------------------------|
| Standard 1 | Ba (0.5), Mn (0.5), Zn (0.5), Sr (0.5) |
| Standard 2 | Ba (1.0), Fe (1.0), Mn (1.0), Zn (2.0), Sr (5.0) |
| Standard 3 | Mg (5.0), Fe (5.0) |
| Standard 4 | Mg (25.0), Na (25.0), Ca (25.0) |
| Standard 5 | Na (100), Ca(100), K (100) |
| Standard 6 | K (200) |
| Standard 7 | S (10.0), P (50.0) |
| Standard 8 | S (50.0), P (150.0) |
| Standard 9 | S (100.0), P (200.0), Ca (250.0) |
| Standard 10 | Ca (1000) |
| Standard 11 | K (1000) |
| Standard 12 | Na (1000) |

Rinse and calibration blank solutions were prepared from 18 M Ω Milli-Q water with 0.5% HNO₃ and 0.002% Triton X100.

Sample Preparation

Solutions were prepared from samples supplied by the Ministry of Agriculture and Fisheries (MAF), New Zealand and SRM 8435 Whole Milk Powder.

Milk powder suspensions containing 2% w/v were prepared for all samples. The sample was accurately weighed and then transferred into a volumetric flask. The flask was filled approximately 3/4 full with 18 M Ω Milli-Q water and gently shaken until the milk powder was evenly mixed. Triton X100 was added to give a concentration of 0.002%. Acid was not added to the samples as it causes the precipitation of protein.

The samples were made up to the mark and placed in an ultrasonic bath for 5 minutes. The samples were then shaken vigorously for 1 minute.

A separate rinse containing 0.002% v/v Triton X100 and no acid was used for rinsing between samples.

Both caesium and scandium were used as internal standards in the analysis. Caesium also acted as an ionization suppressant. A bulk solution of 1% CsCl and scandium (0.5 mg/L) and was added to all solutions via the third channel of the peristaltic pump.

Results and Discussion

Milk Powder Analysis

The results presented in Tables 3–5 represent the concentrations of constituent elements in the milk powder on a dry weight basis. Previous work [2] had shown that the milk powder samples typically have low moisture contents and the samples were determined directly from the raw material without drying.

Table 3. Analysis of Standard Reference Material, S.R.M. 8435

| Element | Wavelength (nm) | 2.0% S.R.M. 8435 whole milk powder (ppm) | S.R.M. 8435 certified value (ppm) |
|---------|-----------------|------------------------------------------|-----------------------------------|
| Ba | 493.408 | 0.72 ± 0.03 | 0.58 ± 0.23 |
| Ca | 373.690 | 8990 ± 340 | 9220 ± 490 |
| K | 404.721 | 12580 ± 210 | 13630 ± 470 |
| Fe | 238.204 | 1.07 ± 0.01 | 1.80 ± 1.1 |
| Mg | 285.213 | 838 ± 27 | 814 ± 76 |
| Mn | 257.610 | 0.17 ± 0.02 | 0.17 ± 0.05 |
| Na | 588.995 | 3810 ± 40 | 3560 ± 400 |
| P | 185.878 | 7400 ± 300 | 7800 ± 490 |
| S | 180.669 | 2320 ± 90 | 2650 ± 400 |
| Sr | 407.771 | 4.10 ± 0.20 | 4.35 ± 0.50 |
| Zn | 202.548 | 25.2 ± 0.9 | 28.0 ± 3.1 |

Table 4. Analysis of 2% Milk Powder

| Element | Wavelength (nm) | 2.0% Milk powder sample (wt%) |
|---------|-----------------|-------------------------------|
| Ba | 493.408 | 0.97 |
| Ca | 373.690 | 8909 |
| K | 404.721 | 11657 |
| Fe | 238.204 | 1.76 |
| Mg | 285.213 | 796 |
| Mn | 257.610 | 0.37 |
| Na | 588.995 | 3118 |
| P | 185.878 | 7729 |
| S | 180.669 | 2278 |
| Sr | 407.771 | 5.48 |
| Zn | 202.548 | 28.4 |

Table 5. Analysis of MAF#1

The “Known values” are values supplied by the New Zealand Dairy Research Institute.

| Element | Wavelength (nm) | 2.0% MAF#1 sample (ppm) | Known value (ppm) |
|---------|-----------------|-------------------------|-------------------|
| Ba | 493.408 | 3.24 ± 0.01 | – |
| Ca | 373.690 | 13750 ± 9 | 13274 |
| K | 404.721 | 15600 ± 120 | 17040 |
| Fe | 238.204 | 1.36 ± 0.04 | 2.0 |
| Mn | 257.610 | 0.310 ± 0.0001 | – |
| Na | 588.995 | 4000 ± 50 | 3490 |
| P | 185.878 | 10600 ± 140 | 9930 |
| S | 180.669 | 3280 ± 40 | 3280 |
| Sr | 407.771 | 3.99 ± 0.03 | – |
| Zn | 202.548 | 40.2 ± 0.8 | 37.33 |

Summary

The concentrations of various elements of both nutritional and environmental interest in milk powder samples were determined directly using the axially viewed Vista simultaneous ICP-OES. Aqueous calibration solutions were used and the scandium and caesium internal standards successfully corrected for the viscosity effects of the samples.

The addition of caesium as an ionization suppressant eliminated ionization interferences and the need for dilution, allowing both major and minor constituents to be measured in a single solution. Both trace and major element concentrations were able to be determined in the 2% w/v milk powder samples, with less sensitive analytical lines chosen for the elements present in the greatest concentrations, such as Ca. This wavelength selection flexibility, provided by the optical and detector design of the Vista, avoided the need to re-measure samples using the less sensitive radial optical configuration.

All measured values are in very good agreement with the certified values for the standard reference material, validating the accuracy of the method.

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